

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 506 788 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
16.02.2005 Bulletin 2005/07

(51) Int Cl.7: **A61L 15/60, A61F 13/15,
C08J 3/28**

(21) Application number: **03017940.2**

(22) Date of filing: **06.08.2003**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(72) Inventor: **Flohr, Andreas**
61476 Kronberg (DE)

(74) Representative: **Borbach, Markus et al**
Procter & Gamble Service GmbH,
Sulzbacher Strasse 40-50
65823 Schwalbach am Taunus (DE)

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

(54) **Superabsorbent polymers having radiation activatable surface cross-linkers and method of making them**

(57) The present invention relates to superabsorbent polymer particles with improved surface cross-linking and their use in absorbent articles.

The superabsorbent polymer particles of the present invention comprise a water-absorbing resin and a radiation activatable surface cross-linker wherein the radiation activatable surface cross-linker is present at

surfaces of the superabsorbent polymer particles. The radiation activatable surface cross-linker comprises at least two radiation activatable groups R, which are covalently bound to at least one spacer group S.

Moreover, the invention relates to a process for making these superabsorbent polymer particles.

EP 1 506 788 A1

Description**Field of the invention**

5 [0001] The present invention relates to superabsorbent polymer particles with improved surface cross-linking and their use in absorbent articles.

[0002] Moreover, the invention relates to a process for making these superabsorbent polymer particles.

Background of the invention

10

[0003] Superabsorbent polymers (SAPs) are well known in the art. They are commonly applied in absorbent articles, such as diapers, training pants, adult incontinence products and feminine care products to increase the absorbent capacity of such products while reducing their overall bulk. The SAPs generally are capable of absorbing and retaining amounts of aqueous fluids equivalent to many times their own weight.

15

[0004] Commercial production of SAPs began in Japan in 1978. The early superabsorbent was a cross-linked starch-g-polyacrylate. Partially neutralized polyacrylic acid eventually replaced earlier superabsorbents in the commercial production of SAPs, and is the primary polymer employed for SAPs today. SAPs are often applied in form of small particles, such as fibers or granules. They generally consist of a partially neutralized lightly cross-linked polymer network, which is hydrophilic and permits swelling of the network once submerged in water or an aqueous solution such as physiological saline. The cross-links between the polymer chains assure, that the SAP does not dissolve in water.

20

[0005] After absorption of an aqueous solution, swollen SAP particles become very soft and deform easily. Upon deformation the void spaces between the SAP particles are blocked, which drastically increases the flow resistance for liquids. This is generally referred to as "gel-blocking". In gel blocking situations liquid can move through the swollen SAP particles only by diffusion, which is much slower than flow in the interstices between the SAP particles.

25

[0006] One commonly applied way to reduce gel blocking is to make the particles stiffer, which enables the SAP particles to retain their original shape thus creating or maintaining void spaces between the particles. A well-known method to increase stiffness is to cross-link the carboxyl groups exposed on the surface of the SAP particles. This method is commonly referred to as surface cross-linking.

30

[0007] European Patent EP 0 509 708 B1 refers to surface cross-linked and surfactant coated absorbent resin particles and a method of their preparation. The surface cross-linking agent in EP 0 509 708 B1 is a polyhydroxyl compound comprising at least two hydroxyl groups, which react with the carboxyl groups on the surface of the SAP particles. In EP 0 509 708 B1, surface cross-linking is carried out at temperatures of 150°C or above. The particles are preferably exposed to the elevated temperatures for at least 5 minutes but less than 60 minutes.

35

[0008] U.S. Patent 5,164,459 discloses another method for surface cross-linking absorbent resins, wherein the carboxyl groups of the polymer, which are comprised on the surface of the resin, react with a polyhydric alcohol. The reaction is accomplished at temperatures in the range of 90°C to 250°C.

[0009] In WO 01/89591 A2 hydroxyalkylurea is used as cross-linking agent. WO 01/89592 applies hydroxyalkylamide as cross-linking agent. In both applications, the surface cross-linking reaction is carried out at temperatures from about 90°C to about 170°C for 60 to 180 minutes.

40

[0010] A water-soluble peroxide radical initiator as surface cross-linking agent is known from European Patent Application EP 0 248 437 A2. An aqueous solution containing the surface cross-linking agent is applied on the surface of the polymer. The surface cross-linking reaction is achieved by heating to a temperature such that the peroxide radical initiator is decomposed while the polymer is not decomposed.

45

[0011] European Patent Application EP 1 199 327 A2 discloses the use of an oxetane compound and / or an imidazolidinone compound for use as surface cross-linking agent. The surface cross-linking reaction is carried out under heat, wherein the temperature is preferably in the range of 60°C to 250°C. Alternatively, the surface cross-linking reaction in EP 1 199 327 A2 is achieved by a photo-irradiation treatment, preferably using ultraviolet rays.

50

[0012] In general, the surface cross-linking agent is applied on the surface of the SAP particles. Therefore, the reaction preferably takes place on the surface of the SAP particles, which results in improved cross-linking on the surface of the particles while not substantially affecting the core of the particles. Hence, the SAP particles become stiffer and gel-blocking is reduced.

55

[0013] A drawback of the commercial surface cross-linking process described above is, that it takes relatively long, commonly at least about 30 min. However, the more time is required for the surface cross-linking process, the more surface cross-linking agent will penetrate into the SAP particles, resulting in increased cross-linking inside the particles, which has a negative impact on the capacity of the SAP particles. Therefore, it is desirable to have short process times for surface cross-linking. Furthermore, short process times are also desirable with respect to an overall economic SAP particle manufacturing process.

[0014] Another drawback of common surface cross-linking processes is, that they takes place only under relatively

high temperatures, often around 150 °C or above. At these temperatures, not only the surface cross-linker reacts with the carboxyl groups of the polymer, but also other reactions are activated, e.g. anhydride-formation of neighbored carboxyl groups within or between the polymer chains, and dimer cleavage of acrylic acid dimers incorporated in the SAP particles. Those side reactions also affect the core, decreasing the capacity of the SAP particles. In addition, exposure to elevated temperatures can lead to color degradation of the SAP particles. Therefore, these side reactions are generally undesirable.

[0015] SAPs known in the art are typically partially neutralized, e.g. with sodium hydroxide. However, neutralization has to be carefully balanced with the need for surface cross-linking: The surface cross-linking agents known in the art only react with free carboxyl groups comprised by the polymer chains but they are not able to react with a neutralized carboxyl groups. Thus, the carboxyl groups can either be applied for surface cross-linking or for neutralization, but the same carboxyl group cannot be applied to fulfill both tasks. Surface cross-linking agents known in the art do not react with chemical groups other than carboxyl groups, e.g. they do not react with aliphatic groups.

[0016] In the process of making SAP particles, neutralization of free carboxyl groups typically comes first, before surface cross-linking takes place. Indeed, the neutralization step is often carried out in the very beginning of the process, before the monomers are polymerized and cross-linked to form the SAP. Such a process is named 'pre-neutralization process'. Alternatively, the SAP can be neutralized in the middle of polymerization or after polymerization ('post-neutralization'). Furthermore, a combination of these alternatives is also possible.

[0017] As the overall number of free carboxyl groups on the outer surface of the SAP particles is limited by the foregoing neutralization, it is very difficult to obtain particles with a high degree of surface cross-linking and hence, a high stiffness to reduce gel-blocking. Furthermore, it is very difficult to obtain SAP particles with evenly distributed surface cross-linking, as the remaining free carboxyl groups are not only few in number but generally also randomly distributed, which sometimes results in SAP particles with regions of rather dense surface cross-linking and regions of sparsely surface cross-linking.

[0018] It is therefore an objective of the present invention to provide SAP particles, which have a high degree of surface cross-linking and at the same time allow for a high degree of neutralization.

[0019] It is a further objective of the present invention to provide SAP particles with evenly distributed, homogenous surface cross-linking.

[0020] Furthermore, it is an objective of the present invention to provide a process to produce SAP particles with the above-mentioned advantages.

[0021] It is a still further objective of the present invention to provide a process to produce SAP particles, wherein the process step of surface cross-linking can be carried out quickly to increase the efficiency of the process.

[0022] Moreover, a further objective of the present invention is to provide a process to produce SAP particles, which can be carried out at moderate temperatures in order to reduce undesired side reactions, such as anhydride-formation and dimer cleavage.

Summary of the invention

[0023] The present invention relates to superabsorbent polymer particles comprising a water-absorbing resin and a radiation activatable surface cross-linker wherein the radiation activatable surface cross-linker is present at surfaces of the superabsorbent polymer particles. The radiation activatable surface cross-linker comprises at least two radiation activatable groups R, which are covalently bound to each other or to at least one spacer group S.

[0024] The spacer group S is selected from the group comprising an organic group with a molecular weight of up to $M_w=10000$, and a polymeric group with a molecular weight of up to $M_w=1000000$.

[0025] The radiation activatable group R can be selected from the group comprising acetophenone, benzophenone, acetophenone-, benzophenone-, anthraquinone-, thioxanthone-, and xanthone-derivatives and acetophenone- or benzophenone-derivatives, wherein acetophenone derivatives or benzophenone derivatives also comprise reaction products, such as condensation products, of acetophenone derivatives or benzophenone derivatives, comprising at least two acetophenone or benzophenone groups.

[0026] Alternatively, the radiation activatable group R comprises a first group selected from the group comprising methyl, benzyl, aryl, preferably phenyl and substituted phenyl, and the radiation activatable group R further comprises a second group selected from the group comprising an aryl, an alkyl of 1 to 4 carbon atoms, cyclopropyl, cyclopentyl, cyclohexyl, α,α -dialkoxyalkyl, and α -hydroxyalkyl and wherein the first group is covalently bound to the second group via an additional carbonyl group, and wherein the second group is covalently bound to the spacer group S.

[0027] The radiation activatable surface cross-linker comprises either only one kind of radiation activatable group OF-comprises two or more different radiation activatable groups. The radiation activatable surface cross-linker comprises optionally either only one kind of spacer group S or comprises two or more different spacer groups S.

[0028] The present invention further relates to a method of making superabsorbent polymer particles which comprises the steps of

- a) providing a water-absorbing resin
- b) adding radiation activatable surface cross-linkers
- 5 c) exposing said water-absorbing resin and said radiation activatable surface cross-linkers to electromagnetic radiation

wherein the radiation activatable surface cross-linker is a radiation activatable surface cross-linker as described above.

10 Detailed description of the invention

[0029] The SAPs according to the present invention comprise a homopolymer of partially neutralized α,β -unsaturated carboxylic acid or a copolymer of partially neutralized α,β -unsaturated carboxylic acid copolymerized with a monomer copolymerizable therewith. Furthermore, the homo-polymer or copolymer comprised by the SAP comprises aliphatic groups, wherein at least some of the aliphatic groups are at least partially exposed on the surface of the superabsorbent polymer particles

[0030] SAPs are available in a variety of chemical forms, including substituted and unsubstituted natural and synthetic polymers, such as carboxymethyl starch, carboxymethyl cellulose, and hydroxypropyl cellulose; nonionic types such as polyvinyl alcohol, and polyvinyl ethers; cationic types such as polyvinyl pyridine, polyvinyl morpholinone, and N,N-dimethylaminoethyl or N,N-diethylaminopropyl acrylates and methacrylates, and the respective quaternary salts thereof. Typically, SAPs useful herein have a multiplicity of anionic, functional groups, such as sulfonic acid, and more typically carboxyl groups. Examples of polymers suitable for use herein include those, which are prepared from polymerizable, unsaturated, acid-containing monomers. Thus, such monomers include the olefinically unsaturated acids and anhydrides that contain at least one carbon-to-carbon olefinic double bond. More specifically, these monomers can be selected from olefinically unsaturated carboxylic acids and acid anhydrides, olefinically unsaturated sulfonic acids, and mixtures thereof.

[0031] Some non-acid monomers can also be included, usually in minor amounts, in preparing SAPs. Such non-acid monomers can include, for example, the water-soluble or water-dispersible esters of the acid-containing monomers, as well as monomers that contain no carboxylic or sulfonic acid groups at all. Optional non-acid monomers can thus include monomers containing the following types of functional groups: carboxylic acid or sulfonic acid esters, hydroxyl groups, amide-groups, amino groups, nitrile groups, quaternary ammonium salt groups, aryl groups (e.g., phenyl groups, such as those derived from styrene monomer). These non-acid monomers are well-known materials and are described in greater detail, for example, in U.S. Patent 4,076,663 and in U.S. Patent 4,062,817.

[0032] Olefinically unsaturated carboxylic acid and carboxylic acid anhydride monomers include the acrylic acids typified by acrylic acid itself, methacrylic acid, ethacrylic acid, α -chloroacrylic acid, α -cyanoacrylic acid, β -methylacrylic acid (crotonic acid), α -phenylacrylic acid, β -acryloxypropionic acid, sorbic acid, α -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, β -styrylacrylic acid, itaconic acid, citroconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene and maleic acid anhydride.

[0033] Olefinically unsaturated sulfonic acid monomers include aliphatic or aromatic vinyl sulfonic acids such as vinylsulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid and styrene sulfonic acid; acrylic and methacrylic sulfonic acid such as sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid and 2-acrylamide-2-methylpropane sulfonic acid.

[0034] Preferred SAPs according to the present invention contain carboxyl groups. These polymers comprise hydrolyzed starch-acrylonitrile graft copolymers, partially neutralized hydrolyzed starch-acrylonitrile graft copolymers, starch-acrylic acid graft copolymers, partially neutralized starch-acrylic acid graft copolymers, saponified vinyl acetate-acrylic ester copolymers, hydrolyzed acrylonitrile or acrylamide copolymers, slightly network crosslinked polymers of any of the foregoing copolymers, partially neutralized polyacrylic acid, and slightly network crosslinked polymers of partially neutralized polyacrylic acid, partially neutralized polymethacrylic acid, and slightly network crosslinked polymers of partially neutralized polymethacrylic acid. These polymers can be used either solely or in the form of a mixture of two or more different polymers, that when used as mixtures, individually do not have to be partially neutralized, whereas the resulting copolymer has to be. Examples of these polymer materials are disclosed in U.S. Patent 3,661,875, U.S. Patent 4,076,663, U.S. Patent 4,093,776, U.S. Patent 4,666,983, and U.S. Patent 4,734,478.

[0035] Most preferred polymer materials for use herein are slightly network crosslinked polymers of partially neutralized polyacrylic acids, slightly network crosslinked polymers of partially neutralized polymethacrylic acids, their copolymers and starch derivatives thereof. Most preferably, SAPs comprise partially neutralized, slightly network crosslinked, polyacrylic acid (i.e. poly (sodium acrylate/acrylic acid)). Preferably, the SAPs are at least 50%, more preferably at least 70%, even more preferably at least 75% and even more preferably from 75% to 95% neutralized. Network crosslinking renders the polymer substantially water-insoluble and, in part, determines the absorptive capacity of the

hydrogel-forming absorbent polymers. Processes for network crosslinking these polymers and typical network crosslinking agents are described in greater detail in U.S. Patent 4,076,663.

[0036] A suitable method for polymerizing the α,β -unsaturated carboxylic acid monomers is aqueous solution polymerization, which is well known in the art. An aqueous solution comprising α,β -unsaturated carboxylic acid monomers and polymerization initiator is subjected to a polymerization reaction. The aqueous solution may also comprise further monomers, which are co-polymerizable with the α,β -unsaturated carboxylic acid monomers. At least the α,β -unsaturated carboxylic acid has to be partially neutralized, either prior to polymerization of the monomers, during polymerization or post polymerization. In a preferred embodiment of the present invention, the monomers (including α,β -unsaturated carboxylic acid monomers and possible comonomers) are at least 50 %, more preferably at least 70%, even more preferably at least 75% and even more preferably from 75% to 95% neutralized.

[0037] The monomers in aqueous solution are polymerized by standard free radical techniques, commonly by using a photoinitiator for activation, such as ultraviolet (UV) light. Alternatively, a redox initiator may be used. In this case, however, increased temperatures are necessary.

[0038] The water-absorbent resin will preferably be lightly cross-linked to render it water-insoluble. The desired cross-linked structure may be obtained by the co-polymerization of the selected water-soluble monomer and a cross-linking agent possessing at least two polymerizable double bonds in the molecular unit. The cross-linking agent is present in an amount effective to cross-link the water-soluble polymer. The preferred amount of cross-linking agent is determined by the desired degree of absorption capacity and the desired strength to retain the absorbed fluid, that is, the desired absorption under load. Typically, the cross-linking agent is used in amounts ranging from 0.0005 to 5 parts by weight per 100 parts by weight of monomers (including α,β -unsaturated carboxylic acid monomers and possible comonomers) used. If an amount over 5 parts by weight of cross-linking agent per 100 parts is used, the resulting polymer has a too high cross-linking density and exhibits reduced absorption capacity and increased strength to retain the absorbed fluid. If the cross-linking agent is used in an amount less than 0.0005 parts by weight per 100 parts, the polymer has a too low cross-linking density and when contacted with the fluid to be absorbed becomes rather sticky, water-soluble and exhibits a low absorption performance, particularly under load. The cross-linking agent will typically be soluble in the aqueous solution.

[0039] Alternatively to co-polymerizing the cross-linking agent with the monomers, it is also possible to cross-link the polymer chains in a separate process step after polymerization.

[0040] After polymerization, cross-linking and partial neutralization, the viscous SAPs are dehydrated (i.e. dried) to obtain dry SAPs. The dehydration step can be performed by heating the viscous SAPs to a temperature of about 120°C for about 1 or 2 hours in a forced-air oven or by heating the viscous SAPs overnight at a temperature of about 60°C.

[0041] The SAPs can be transferred into particles of numerous shapes. The term "particles" refers to granules, fibers, flakes, spheres, powders, platelets and other shapes and forms known to persons skilled in the art of SAPs. E.g. the particles can be in the form of granules or beads, having a particle size of about 10 to 1000 μm , preferably about 100 to 1000 μm . In another embodiment, the SAPs can be in the shape of fibers, i.e. elongated, acicular SAP particles. In those embodiments, the SAP fibers have a minor dimension (i.e. diameter of the fiber) of less than about 1 mm, usually less than about 500 μm , and preferably less than 250 μm down to 50 μm . The length of the fibers is preferably about 3 mm to about 100 mm. The fibers can also be in the form of a long filament that can be woven.

[0042] According to the present invention the dehydrated SAP particles undergo a surface cross-linking process step. The term "surface" describes the outer-facing boundaries of the particle. For porous SAP particles, exposed internal surfaces may also belong to the surface. The term "surface cross-linked SAP particle" refers to an SAP particle having its molecular chains present in the vicinity of the particle surface cross-linked by a compound referred to as surface cross-linker. The surface cross-linker is applied to the surface of the particle. In a surface cross-linked SAP particle the level of cross-links in the vicinity of the surface of the SAP particle is generally higher than the level of cross-links in the interior of the SAP particle.

[0043] Commonly applied surface cross-linkers are thermally activated surface cross-linkers. The term "thermally activated surface cross-linkers" refers to surface cross-linkers, which only react upon exposure to increased temperatures, typically around 150 °C. Thermally activated surface cross-linkers known in the prior art are e.g. di- or polyfunctional agents that are capable of building additional cross-links between the polymer chains of the SAPs. Other thermally activated surface cross-linkers include, e.g., di- or polyhydric alcohols, or derivatives thereof, capable of forming di- or polyhydric alcohols. Representatives of such agents are alkylene carbonates, ketals, and di- or polyglycidylethers. Moreover, (poly)glycidyl ethers, haloepoxy compounds, polyaldehydes, polyols and polyamines are also well known thermally activated surface cross-linkers. The cross-linking is based on a reaction between the functional groups comprised by the polymer, for example, an esterification reaction between a carboxyl group (comprised by the polymer) and a hydroxyl group (comprised by the surface cross-linker). As typically a relatively big part of the carboxyl groups of the polymer chain is neutralized prior to the polymerization step, commonly only few carboxyl groups are available for this surface cross-linking process known in the art. E.g. in a 70% percent neutralized polymer only 3 out of 10 carboxylic groups are available for covalent surface cross-linking.

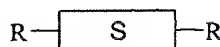
[0044] The present invention relates to radiation activatable surface cross-linkers, the SAP particles obtained from such radiation activated surface cross-linking, methods of preparing such radiation activated surface cross-linked SAP particles and their use in disposable absorbent articles.

[0045] Such radiation activateable surface cross-linkers comprise at least two radiation activateable groups, capable of forming covalent cross-linking bonds upon being impacted by radiation energy. Radiation activateable compounds as such and their synthesis are known in the art, e.g. from European Patent Application EP-A-0 377 191; U.S. Patent 3,214,492; U.S. Patent 3,429,852; U.S. Patent 3,622,848; U.S. Patent 4,304,895; German Patent Application DE-A-3534645 and European Patent Application EP-A-279 475.

[0046] In the present invention it was found that radiation activateable compounds could be used as surface cross-linkers comprising at least two radiation activateable groups R, which are covalently bound to each other or at least one spacer group S. The radiation activatable groups are capable of forming covalent cross-linking bonds upon being impacted by radiation energy. Moreover, the radiation activateable surface cross-linker can function very well for the surface cross-linking of SAP particles to provide superior capacity and permeability properties.

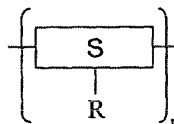
[0047] Formula I shows a preferred embodiment of the radiation activatable surface cross-linker according to the present invention:

Formula I



[0048] Formula II shows another preferred embodiment of the radiation activatable surface cross-linker of the present invention:

Formula II



wherein n is an integer of equal or greater than 2.

[0049] In Formulae II, and I S denotes a spacer group and R denote radiation activateable groups which are able to form organic radicals.

[0050] According to the present invention, the radiation activatable surface cross-linker may comprise only one kind of radiation activatable group R. Alternatively the radiation activatable surface cross-linker may comprise two or more different radiation activatable groups R.

[0051] Furthermore, according to the present invention, the radiation activatable surface cross-linker may comprise only one kind of spacer group S. Alternatively the radiation activatable surface cross-linker may comprise two or more different spacer groups S. In another alternative embodiment, the radiation activatable surface cross-linker does not comprise a spacer.

Radiation activateable groups R

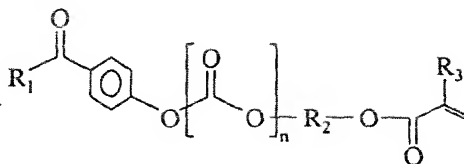
[0052] The radiation activateable groups R are covalently bound to each other or the spacer group S and can be selected from the group comprising acetophenone, benzophenone, acetophenone-, benzophenone-, anthraquinone-, thioxanthone-, and xanthone-derivatives and acetophenone- or benzophenone-derivatives. Suitable acetophenone derivatives or benzophenone derivatives also comprise reaction products, such as condensation products, of acetophenone derivatives or benzophenone derivatives, comprising at least two acetophenone or benzophenone groups.

[0053] Particularly preferred radiation activateable groups R are acetophenone- or benzophenone-derivatives.

[0054] Suitable acetophenone derivatives or benzophenone derivatives are described, for example, in European Patent Application EP-A-0 346 734; European Patent Application EP-A-0 377 199; European Patent Application EP-A-0 246 848; German Patent Application DE-A-4 037 079 and German Patent Application DE-A-3 844 444.

[0055] Preferred acetophenone derivatives and benzophenone derivatives have the general Formula III:

Formula III



wherein

n is 0 or 1, and

R_1 is substituted or unsubstituted phenyl or C_1 - C_4 -alkyl or an ethylenically unsaturated group, preferably comprising an acrylic or methacrylic group, and

R_2 is an organic group having from 1 to 100 carbon atoms, which may be interrupted by up to 49 oxygen atoms, and

R_3 is a hydrogen atom or methyl.

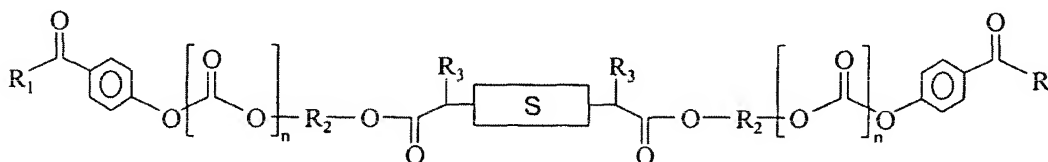
R_2 is preferably an organic group having between 4 and 60 carbon atoms, which may be interrupted by between 1 and 29 oxygen atoms, in particular having between 10 and 40 carbon atoms which may be interrupted by between 4 and 19 oxygen atoms.

R_1 is particularly preferably methyl or phenyl.

R_2 is particularly preferably alkylene, in particular C_2 - C_8 -alkylene.

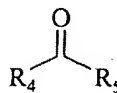
[0056] The preferred acetophenone derivatives and benzophenone derivatives according to Formula III can be covalently bound to a spacer group S to form a radiation activateable surface cross-linker as depicted in Formula IV:

Formula IV



[0057] Alternatively, according to the present invention the radiation activateable groups R have the form according to Formula V:

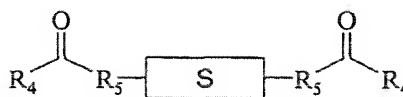
Formula V



wherein R_4 is selected from the group comprising methyl, benzyl, aryl, preferably phenyl and substituted phenyl and R_5 is selected from the group comprising an aryl, an alkyl of 1 to 4 carbon atoms, cyclopropyl, cyclopentyl, cyclohexyl, α,α -dialkoxyalkyl, and α -hydroxyalkyl and wherein R_5 is covalently bound to the spacer group S .

[0058] Two of the radiation activateable group R according to Formula V can be covalently bound to a spacer group S to form a radiation activateable surface cross-linker as depicted in Formula VI:

Formula VI



The spacer group S

[0059] The spacer group S is selected from the group comprising an organic group and a polymeric group. If the spacer group S is an organic group, the organic group has a molecular weight of up to Mw = 10000, preferably up to 1000. Alternatively, the spacer group S, for example, comprises up to 100 carbon atoms. If the spacer group S is a polymeric group, the polymeric group has a molecular weight up to Mw = 1000000, preferably from 5000 to 600000, more preferably from 10000 to 500000 and particularly preferably from 30000 to 250000. If the radiation activatable surface cross-linker comprises a spacer group S, the spacer group S is covalently bound to the radiation activatable groups R.

[0060] If the spacer group S is a polymeric group, then such polymer has preferably been built up from free-radical polymerizable compounds (= comonomers). At least 40% by weight of the polymer, particularly preferably at least 60% by weight, very particularly preferably at least 80% by weight, is composed of the comonomers.

[0061] In a preferred embodiment of the present invention, the comonomers may comprise the following groups as part of a monomer molecule: carboxylic acid, sulfonic acid, phosphonic acid or hydroxyl. Carboxylic and sulfonic acid groups are preferred.

[0062] Typically, but not limiting, examples for such preferable monomer-units according to the present invention are: acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, vinylsulfonic acid, allylsulfonic acid, acrylamidomethanpropane sulfonic acid, vinylalcohol, vinylamine, allylamine, polyethyleneglycolemonoacrylate, polyethyleneglycolediacylate, polyethyleneglycolemonoallyether, polyethyleneglycolediiallyether, ethoxylated trimethylolpropane-triacrylate, ethylene, propylene, vinyl chloride, aziridine, isobutylene, styrene, isoprene, acrylonitrile, ethyl acrylate, butyl acrylate, maleic acid anhydride, maleic acid esters, methylmethacrylate, vinyl acrylate, allylmethacrylate, allylsulfonate, vinyl sulfonate, acrylamide, methacrylamide, acrylamidomethylpropanesulfonate (AMPS), C₁-C₄-hydroxyalkyl methacrylate, C₁-C₄-hydroxyalkyl acrylate, tripropylene glycol diacrylate, trimethylol propane ethoxylated triacrylate, epoxy acrylates, ethylene oxide, propylene oxide, polyester acrylates, urethane acrylates, C₁-C₂₀-alkyl methacrylates, vinyl esters of carboxylic acids containing up to 20 carbon atoms, vinyl aromatics having up to 20 carbon atoms, ethylenically unsaturated nitriles, vinyl halides, vinyl ethers of alcohols containing from 1 to 10 carbon atoms, aliphatic hydrocarbons having from 2 to 8 carbon atoms and 1 or two double bonds, and mixtures of these monomers.

[0063] Examples of vinyl esters of carboxylic acids having from 1 to 20 carbon atoms are vinyl laurate, vinyl stearate, vinyl propionate, vinyl versates and vinyl acetate.

[0064] Possible vinyl aromatics compounds are vinyl toluene, α- and p-methylstyrene, α-butylstyrene, 4-n-butylstyrene, 4-n-decylstyrene and, preferably, styrene. Examples of nitriles are acrylonitrile and methacrylonitrile.

[0065] Vinyl halides are chlorine-, fluorine- or bromine-substituted ethylenically unsaturated compounds, preferably vinyl chloride and vinylidene chloride.

[0066] Examples of vinyl ethers, are vinyl methyl ether and vinyl isobutyl ether. Preference is given to vinyl ethers of alcohols containing from 1 to 4 carbon atoms.

[0067] As hydrocarbons having from 2 to 8 carbon atoms and two olefinic double bonds, mention should be made of butadiene, isoprene, and chloroprene.

[0068] The comonomers may also be copolymerized with a precursor molecule of the comonomers. Examples of preferred precursors are vinylformamid, vinylacetate, vinylacetamide, all of which will have to be finally hydrolyzed after the polymerization in order to incorporate the corresponding monomer units, vinylamine and vinylalcohol.

Process

[0069] Above-mentioned radiation activatable surface cross-linkers are capable to form covalent bonds by exposure to electromagnetic radiation. Electron beams as well as UV-light can produce suitable electromagnetic radiation. Preferably, according to the present invention UV-light is used with a wave-length of 220-340 nm, most preferably with a wave-length between 220-290 nm. The UV-light may be used in combination with an electron-beam, and also in combination with an IR-light. In case of combination of UV-irradiation with other electromagnetic radiation, it is not critical if the application of the UV-light takes place simultaneously with the other electromagnetic irradiation (i.e. electron-

beam or IR-light), or if irradiation is done in a series of different irradiation steps. For radiation activatable surface cross-linkers, which require a relative high amount of activation energy, activation with electron beams may be necessary.

[0070] In the present invention the radiation activatable surface cross-linker is applied in amounts of less than 50% by weight of SAP particle, preferably in amounts of less than 25%, more preferably in amounts of less than 15%, even

more preferably in amounts of less than 5% and most preferably in amounts from 0.1% to 5%.

[0071] The novel radiation activatable surface cross-linker may be sprayed onto the SAP particles by means of a fluidized-bed spraying chamber. Simultaneously IR-irradiation may be applied to accomplish drying and simultaneously UV-light may be applied to accomplish cross-linking in the fluidized-bed.

[0072] However, in certain cases drying and cross-linking may take place in two steps in series, which could be carried out in any order. Instead or in combination with IR-light, any conventional drying equipment can be used in the drying step. However, in certain embodiments of the present invention little or no drying is required, e.g. in cases, where only small amounts of surface cross-linkers are applied dissolved in small amounts of solution.

[0073] The surface cross-linking of the SAP particles with the radiation activatable surface cross-linker according to the present invention effectively takes place at the photo-reactive groups of the radiation activatable surface cross-linker, forming covalent bonds. On exposure to electromagnetic radiation, most preferably UV-irradiation, a covalent bond is formed by means of the chemical grafting reaction.

[0074] In particular, the surface cross-linking may take place by reaction of an electromagnetic radiation activated photo-reactive group of the novel surface cross-linker with an adjacent aliphatic C-H bond, forming a -C-C-O-H group in case the photo-reactive group of the surface cross-linker is a carboxyl group. The aliphatic C-H bond, may be part of a nearby polymer chain. The polymer chain may be another radiation activatable surface cross-linker molecule, a part of the same cross-linker molecule or may be part of the polymer chain of the SAP particles exposed to the surface of such SAP particles.

[0075] Therefore, at least a part of the surface cross-linker molecules form radicals, which are able to react with the functional groups (e.g. carboxyl group) comprised by the polymer and they are also able to react e.g. with the aliphatic groups comprised by the polymer. As a result of this reaction at least a part of the surface cross-linker molecules are covalently bonded to the aliphatic groups comprised by the polymer chains of the SAP particles. Alternatively, it is also possible that the surface cross-linker molecules are covalently bound to at least a part of the carboxyl groups of the polymer chains of the SAP particles. The surface cross-linker will mainly be bound to those carboxyl groups, which are at least partially exposed on the surface of the SAP particles. However, compared to prior art surface cross-linking, the cross-linking process of the present invention is not restricted to the carboxyl groups but also comprises the numerous aliphatic groups within the polymer chains of the SAP. Hence, according to the present invention the number of available reaction sites for the surface cross-linking process of the SAP particles is strongly increased. Therefore, it is possible to achieve a far more homogenous, uniform surface cross-linking compared to the surface cross-linking known from the art. Furthermore, it is possible to surface cross-link the SAP to a higher degree than the SAP known from the prior art. This enables to make the SAP particles much stiffer, thus, to more effectively inhibit the gel-blocking effect at a given degree of neutralization. Moreover, it is possible to increase the capacity of the SAP particles.

[0076] As the surface cross-linker is applied on the surface of the SAP particles, the reaction takes mainly place on the surface of the SAP particles. That means, that mainly aliphatic groups and/or functional groups, which are exposed in the vicinity of the surface of the SAP particles, undergo a cross-linking process, leading to SAP particles with a high degree of cross-linking on their surface while not substantially affecting the inner core of the SAP particles. Hence, the percentage of the radiation activatable surface cross-linker on the surface of said superabsorbent polymer particles will preferably be higher than the percentage of the radiation activatable surface cross-linker inside the superabsorbent polymer particles.

[0077] The UV radiation for the surface cross-linking is preferably carried out at intensities of 10 to 300 W/cm, more preferably 10 to 200 W/cm, even more preferred 10 to 150 W/cm and most preferred 10 to 120 W/cm preferably for 0.0001 sec. to 30 min., more preferably from 0.0001 sec. to 15 min, even more preferably 0.0001 sec. to 5 min and most preferably 0.0001 sec. to 2 min. Commercially available mercury pressure UV-lamps can be used.

[0078] Compared to the surface cross-linking known from the prior art, the surface cross-linking according to the present invention is much quicker. Prior art surface cross-linking reactions carried out under increased temperatures commonly take up to 45 minutes. This time consuming process step renders the manufacturing process of SAP particles less economic than desirable. On the contrary, the cross-linking process according to the present invention can be carried out very quick and hence, strongly adds to a much more efficient and economic overall manufacturing process.

[0079] Furthermore, as the surface cross-linking reaction proceeds quickly, the surface cross-linking molecules applied on the surface of the SAP particles have less time to penetrate inside the SAP particles. As a result, the surface cross-linking process is mainly restricted to the surface of the SAP particles and avoids undesired further cross-linking reactions inside the SAP particles.

[0080] Another advantage of the present invention refers to the neutralization step. The α,β -unsaturated carboxylic acid monomers are often neutralized prior to the polymerization step (pre-neutralization). Compounds, which are useful

to neutralize the acid groups of the monomers, are typically those, which will sufficiently neutralize the acid groups without having a detrimental effect on the polymerization process. Such compounds include alkali metal hydroxides, alkali metal carbonates and bicarbonates. Preferably, the material used for neutralization of the monomers is sodium or potassium hydroxide or carbonate. The neutralizing compound is preferably added to an aqueous solution comprising the α,β -unsaturated carboxylic acid monomers (pre-neutralization). As a result, the carboxyl groups comprised by the α,β -unsaturated carboxylic acid monomers are at least partially neutralized. Consequently, -after the polymerization step- also the carboxyl groups comprised by the α,β -unsaturated carboxylic acid of the polymer are at least partially neutralized. In case sodium hydroxide is used, neutralization results in sodium acrylate, which dissociates in water into negatively charged acrylate monomers and positively charged sodium ions.

[0081] If the final SAP particles are in the swollen state, after they absorbed aqueous solution, the sodium ions are freely movable within the SAP particles. In absorbent articles, such as diapers or training pants, the SAP particles typically absorb urine. Compared to distilled water, urine comprises a relatively high amount of salt, which at least partly is present in dissociated form. The dissociated salts comprised by the urine make absorption of liquid into the SAP particles more difficult, as the liquid has to be absorbed against an osmotic pressure caused by the ions of the dissociated salts. The freely movable sodium ions within the SAP particles strongly facilitate the absorption of liquid into the particles, because they reduce the osmotic pressure. Therefore, a high degree of neutralization can largely increase the capacity of the SAP particles and the speed of liquid absorption.

[0082] The surface cross-linkers known in the art react with the carboxyl groups of the polymer. Hence, the degree of neutralization has to be balanced with the need to surface cross-link, because both process steps make use of the carboxyl groups.

[0083] According to the present invention, the surface cross-linker comprises radiation activatable groups and -once activated e.g. by UV radiation- it is able to react not only with the carboxyl groups but also with the aliphatic groups comprised by the polymer. Therefore, it is possible to neutralize the monomers to a larger degree without significantly diminishing the possibility of later surface cross-linking.

[0084] According to the present invention, the carboxyl groups comprised by the α,β -unsaturated carboxylic acid monomers are preferably at least 50 %, more preferably at least 70%, even more preferably at least 75% and even more preferably between 75% and 95% neutralized. Hence, also the carboxyl groups comprised by the α,β -unsaturated carboxylic acid of the polymer are at least 50 %, more preferably at least 70%, even more preferably at least 75% and even more preferably between 75% and 95% neutralized.

[0085] A still further advantage of the present invention is the reduction of undesired side-reactions during the surface cross-linking process. Surface cross-linking known from the prior art requires increased temperatures, commonly around or above 150°. At these temperatures, not only the surface cross-linking reaction is achieved, but also a number of other reactions take place, e.g. anhydride-formation within the polymer or dimer cleavage of dimers previously formed by the acrylic acid monomers. These side-reactions are highly undesired, because they result in SAP particles with decreases capacity.

[0086] As the surface cross-linking process according to the present invention does not necessarily need increased temperatures but can also be carried out at moderate temperatures using electromagnetic radiation, such as UV radiation, those side-reactions are considerably reduced. According to the present invention, the surface cross-linking reaction can preferably be accomplished at temperatures of less than 100°C, preferably at temperatures less than 80 °C, more preferably at temperatures less than 50 °C, even more preferably at temperatures less than 40 °C, most preferably at temperatures between 20 °C and 40°C. In an additional process step drying of the SAP is typically carried out at temperatures above 100 °C.

[0087] At elevated temperatures around or above 150°C commonly applied in the surface cross-linking process known from the prior art, the SAP particles sometimes change their color from white to yellowish. As according to the surface cross-linking process of the present invention, it is possible to carry out the surface cross-linking process under moderate temperatures, the problem of color degradation of the SAP particles is strongly reduced.

[0088] According to the present invention, one surface cross-linker can be selected or, alternatively, two or more different surface cross-linkers, can be applied, all being radiation activatable surface cross-linkers.

[0089] As a further alternative, one or more surface cross-linkers being radiation activatable surface cross-linker(s) can be applied together with one or more thermally activated surface cross-linkers, e.g. 1,4-butanediol. In this embodiment, the SAP particles further have to comprise carboxyl groups wherein at least some of the carboxyl groups are at least partially exposed on the outer surface of the SAP particles and wherein the thermally activated surface cross-linker is covalently bound to at least a part of the carboxyl groups at least partially exposed on the surface of said superabsorbent polymer particles.

[0090] In case a radiation activatable surface cross-linker is used together with a thermally activated surface cross-linker, both UV radiation and increased temperatures (above 140°C) are necessary for the surface cross-linking process.

[0091] The radiation activatable surface cross-linker is preferably used in a liquid solution, more preferably in an

aqueous solution.

[0092] To obtain SAP particles with evenly distributed surface cross-linking, the surface cross-linker has to be distributed evenly on the SAP particle prior to or during UV radiation. Therefore, the surface cross-linker is preferably applied by spraying onto the SAP particles.

5 [0093] The water-absorbing resin provided for the process is preferably dry SAP particles. Alternatively, the water-absorbing resin is pre-swollen SAP particles. The term "dry SAP particles" refers to SAPs containing from no water up to an amount of less than 5 % by weight of water (wherein 100% by weight is the amount of SAP including the water). The term "pre-swollen SAP particles" refers to SAPs containing from 5% by weight of water up to an amount of 80% by weight of water, preferably up to an amount of 50% by weight of water, more preferably up to an amount of 30% by weight of water.

Absorbent articles

15 [0094] The SAP particles of the present invention are preferably applied in absorbent articles. As used herein, absorbent article refers to devices that absorb and contain liquid, and more specifically, refers to devices that are placed against or in proximity to the body of the wearer to absorb and contain the various exudates discharged from the body. Absorbent articles include but are not limited to diapers, adult incontinent briefs, diaper holders and liners, sanitary napkins and the like.

20 [0095] Preferred absorbent articles of the present invention are diapers. As used herein, "diaper" refers to an absorbent article generally worn by infants and incontinent persons about the lower torso.

[0096] "Disposable" is used herein to describe articles that are generally not intended to be laundered or otherwise restored or reused i.e., they are intended to be discarded after a single use and, preferably, to be recycled, composted or otherwise disposed of in an environmentally compatible manner.

25 [0097] "Disposed" is used to mean that an element(s) is formed (joined and positioned) in a particular place or position as a unitary structure with other elements or as a separate element joined to another element.

[0098] The chassis comprises the main body of the diaper. The chassis comprises an outer covering including a liquid pervious topsheet and a liquid impervious backsheet. The chassis may also include most or the entire absorbent core encased between the topsheet and the backsheet. The chassis preferably further includes side panels, leg cuffs and a waist feature. The leg cuffs and the waist feature typically comprise elastic members. One end portion of the diaper is configured as the front waist region of the diaper. The opposite end portion is configured as the rear waist region of the diaper. The intermediate portion of the diaper is configured as the crotch region, which extends longitudinally between the front and rear waist regions. The crotch region is that portion of the diaper which, when the diaper is worn, is generally positioned between the wearer's legs. The waist regions and may include a fastening system comprising fastening members. The diaper may also include other features as are known in the art including front and rear ear panels, waist cap features, elastics and the like to provide better fit, containment and aesthetic characteristics.

35 [0099] The absorbent core may comprise any absorbent material that is generally compressible, conformable, non-irritating to the wearer's skin, and capable of absorbing and retaining liquids such as urine and other certain body exudates. The absorbent core may comprise a wide variety of liquid-absorbent materials commonly used in disposable diapers and other absorbent articles such as comminuted wood pulp, which is generally referred to as air felt. Examples of other suitable absorbent materials include creped cellulose wadding; melt blown polymers, including co-form; chemically stiffened, modified or cross-linked cellulosic fibers; tissue, including tissue wraps and tissue laminates, absorbent foams, absorbent sponges, absorbent gelling materials, or any other known absorbent material or combinations of materials. The absorbent core may further comprise minor amounts (typically less than 10%) of non-liquid absorbent materials, such as adhesives, waxes, oils and the like. Furthermore, the SAP particles of the present invention can be applied as absorbent materials. The SAP particles of the present invention preferably are present in amounts of at least 50% by weight of the whole absorbent core, more preferably at least 60%, even more preferably at least 75% and still even more preferably at least 90% by weight of the whole absorbent core.

45 [0100] The absorbent core preferably comprises an acquisition system, which comprises an upper acquisition layer facing towards the wearer and a lower acquisition layer. In one preferred embodiment the upper acquisition layer comprises a nonwoven fabric whereas the lower acquisition layer preferably comprises a mixture of chemically stiffened, twisted and curled fibers, high surface area fibers and thermoplastic binding fibers. In another preferred embodiment both acquisition layers are provided from a non-woven material, which is preferably hydrophilic. The acquisition layer preferably is in direct contact with the storage layer.

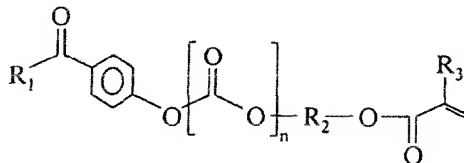
50 [0101] A core wrap material preferably wraps the storage layer. In one preferred embodiment the core wrap material comprises a top layer and a bottom layer, which layers may be sealed together along their edges, e.g. by adhesive. The top layer and the bottom layer can be provided from a non-woven material. The top layer and the bottom layer may be provided from two or more separate sheets of materials or they may be alternatively provided from a unitary sheet of material. Such a unitary sheet of material may be wrapped around the storage layer, e.g. in a C-fold.

[0102] The storage layer the present invention typically comprises SAP particles mixed with fibrous materials. Other materials as suitable for the absorbent core may also be comprised.

5 Claims

1. Superabsorbent polymer particles comprising a water-absorbing resin and a radiation activatable surface cross-linker wherein the radiation activatable surface cross-linker is present at surfaces of the superabsorbent polymer particles, **characterized in that** said radiation activatable surface cross-linker comprises at least two radiation activatable groups R, said at least two radiation activatable groups R being covalently bound to each other or at least one spacer group S,

wherein the spacer group S is a spacer group selected from the group comprising an organic group with a molecular weight of up to $M_w=10000$, and a polymeric group with a molecular weight of up to $M_w=1000000$, and wherein said radiation activatable group R is either selected from the group comprising acetophenone, benzophenone, acetophenone-, benzophenone-, anthraquinone-, thioxanthone-, and xanthone-derivatives and acetophenone- or benzophenone-derivatives, wherein acetophenone derivatives or benzophenone derivatives also comprise reaction products, such as condensation products, of acetophenone derivatives or benzophenone derivatives, comprising at least two acetophenone or benzophenone groups, or wherein said radiation activatable group R is a radiation activatable group R comprising a first group selected from the group comprising methyl, benzyl, aryl, preferably phenyl and substituted phenyl, and said radiation activatable group R further comprises a second group selected from the group comprising an aryl, an alkyl of 1 to 4 carbon atoms, cyclopropyl, cyclopentyl, cyclohexyl, α , α -dialkoxyalkyl, and α -hydroxyalkyl and wherein said first group is covalently bound to said second group via an additional carbonyl group, and wherein the second group comprised by said radiation activatable group R is covalently bound to the spacer group S, and wherein said radiation activatable surface cross-linker comprises either only one kind of radiation activatable group or comprises two or more different radiation activatable groups, and wherein said radiation activatable surface cross-linker optionally comprises either only one kind of spacer group S or comprises two or more different spacer groups S.
2. Superabsorbent polymer particles according to claim 1, wherein said superabsorbent polymer particles comprise homopolymers of partially neutralized α,β -unsaturated carboxylic acid or copolymers of partially neutralized α,β -unsaturated carboxylic acid copolymerized with a monomer copolymerizable therewith, said homopolymers or said copolymers comprising aliphatic groups, wherein at least some of said aliphatic groups are at least partially exposed on the surface of said superabsorbent polymer particles and wherein, said radiation activatable surface cross-linker is covalently bound to at least a part of the aliphatic groups at least partially exposed on the surface of said superabsorbent polymer particles.
3. Superabsorbent polymer particles according to claim 1 or 2, wherein said superabsorbent polymer particles comprise 100 parts by weight of said water absorbing resin and less than 50 parts by weight of said radiation activatable surface cross-linker.
4. Superabsorbent polymer particles according to any of the preceding claims, wherein the percentage of said radiation activatable surface cross-linker on said surface of said superabsorbent polymer particles is higher than the percentage of said radiation activatable surface cross-linker inside said superabsorbent polymer particles.
5. Superabsorbent polymer particles according to any of the preceding claims, wherein radiation activatable groups R are acetophenone derivatives according to the following Formula or benzophenone derivatives according to the following Formula:



wherein

n is 0 or 1, and

R₁ is substituted or unsubstituted phenyl or C₁-C₄-alkyl, or an ethylenically unsaturated group, preferably comprising an acrylic or methacrylic group, and

5 R₂ is an organic radical having from 1 to 100 carbon atoms, which may be interrupted by up to 49 oxygen atoms, and R₃ is a hydrogen atom or methyl.

6. Superabsorbent polymer particles according to any of the preceding claims wherein said superabsorbent polymer particles comprise at least two different radiation activatable surface cross-linkers.

10

7. Superabsorbent polymer particles according to any of the preceding claims wherein said superabsorbent polymer particles further comprise at least one thermally activatable surface cross-linker.

8. Superabsorbent polymer particles according to claim 7 wherein said superabsorbent polymer particles further comprises carboxyl groups wherein at least some of said carboxyl groups are at least partially exposed on the outer surface of said superabsorbent polymer particles and wherein said thermally activatable surface cross-linker is covalently bound to at least a part of said carboxyl groups at least partially exposed on the surface of said superabsorbent polymer particles.

15

9. A method of making superabsorbent polymer particles which comprises the steps of

20

a) providing a water-absorbing resin

b) adding radiation activatable surface cross-linkers

25

c) exposing said water-absorbing resin and said radiation activatable surface cross-linkers to electromagnetic radiation,

wherein said radiation activatable surface cross-linker is a radiation activatable surface cross-linker as claimed in claim 1.

30

10. A method according to claim 9, wherein said superabsorbent polymer particles comprise homopolymers of partially neutralized α,β -unsaturated carboxylic acid or copolymers of partially neutralized α,β -unsaturated carboxylic acid copolymerized with a monomer copolymerizable therewith, said homopolymers or said copolymers comprising aliphatic groups, wherein at least some of said aliphatic groups are at least partially exposed on the surface of said superabsorbent polymer particles and wherein said radiation activatable surface cross-linker reacts to form covalent bonds with at least a part of said aliphatic groups at least partially exposed on the surface of said superabsorbent polymer particle.

35

11. A method according to claims 9 or 10, wherein said electromagnetic radiation is UV radiation.

40

12. A method according to claim 11, wherein said water-absorbing resin and said radiation activatable surface cross-linkers are exposed to UV radiation with an intensity from 10 to 300 W/cm.

13. A method according to claim 12, wherein said water-absorbing resin and said radiation activatable surface cross-linkers are exposed to UV radiation for from 0.0001 seconds to 30 minutes.

45

14. A method according to any of claims 9 to 13, wherein step c) of said method is carried out at temperatures of less than 100 °C.

50

15. A method according to any of claims 9 to 14, wherein said method further comprises the step of drying said superabsorbent polymer particles, said drying being carried out after step c) of claim 9.

16. A method according to any of claims 9 to 15, wherein at least two different radiation activatable surface cross-linkers are added.

55

17. A method according to any of claims 9 to 16, wherein additionally at least one thermally activatable surface cross-linker are added and wherein said method additionally comprises the step of exposing at least said thermally

activatable surface cross-linker and said superabsorbent polymer to temperatures above 140 °C.

- 5 18. A method according to claim 17, wherein said superabsorbent polymer further comprises carboxyl groups wherein at least some of said carboxyl groups are at least partially exposed on the surface of said superabsorbent polymer particle and wherein said thermally activatable surface cross-linker reacts to form covalent bonds with at least a part of said carboxylic groups at least partially exposed on the surface of said superabsorbent polymer particle.
- 10 19. An absorbent article comprising a substantially liquid pervious topsheet, a substantially liquid impervious backsheet and an absorbent core between said topsheet and said backsheet, wherein said absorbent article comprises superabsorbent polymer particles according to any one of claims 1 to 8.
- 15 20. An absorbent article comprising superabsorbent polymer particles, said superabsorbent polymer particles being made according to a process of any one of claims 10 to 18.

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 01 7940

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DATABASE WPI Section Ch, Week 199002 Derwent Publications Ltd., London, GB; Class A14, AN 1990-011701 XP002267035 & JP 01 292103 A (MITSUBISHI RAYON CO LTD) , 24 November 1989 (1989-11-24) * abstract *	1-20	A61L15/60 A61F13/15 C08J3/28
X	US 2003/135172 A1 (ENGELHARDT FRIEDRICH ET AL) 17 July 2003 (2003-07-17) * page 4, right-hand column, line 30 - page 8, right-hand column, line 6 * * page 12, left-hand column, line 32 - right-hand column, line 9 * * page 12, right-hand column, line 36 - line 49 * * page 15, right-hand column, line 34 - page 16, right-hand column, line 7 * * page 19, left-hand column, line 29 - line 35 * * example 1 *	1-20	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	EP 1 264 930 A (PROCTER & GAMBLE) 11 December 2002 (2002-12-11) * column 2, line 13 - column 3, line 22 * * column 4, line 7 - line 10 * * column 4, line 58 - column 7, line 40 * * column 8, line 46 - line 48 * * column 10, line 8 - line 37 * * column 11, line 16 - line 23 * * column 14, line 45 - column 16, line 57 * * claims *	1-20	A61L A61F C08J
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 15 January 2004	Examiner Fey-Lamprecht, F
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03/02 (P04001)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 01 7940

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 6 565 981 B1 (MESSNER BERNFRIED ET AL) 20 May 2003 (2003-05-20) * column 3, line 66 - column 4, line 39 * * column 5, line 29 - column 7, line 41 * * claims * ---	1-3, 6-11, 15-20	
X	EP 0 700 673 A (PROCTER & GAMBLE) 13 March 1996 (1996-03-13) * column 5, line 3 - column 8, line 3 * * column 17, line 22 - line 57 * * column 20, line 43 - column 23, line 4 * * claims; figure 9 * -----	1-4,6-20	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
Place of search MUNICH		Date of completion of the search 15 January 2004	Examiner Fey-Lamprecht, F
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 01 7940

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-01-2004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 1292103	A	24-11-1989	NONE	
US 2003135172	A1	17-07-2003	WO 03053487 A1	03-07-2003
EP 1264930	A	11-12-2002	EP 1264930 A1	11-12-2002
			WO 02101139 A1	19-12-2002
US 6565981	B1	20-05-2003	AU 2821600 A	16-10-2000
			BR 0009506 A	08-01-2002
			CA 2365711 A1	05-10-2000
			CN 1348520 T	08-05-2002
			EP 1173639 A1	23-01-2002
			WO 0058546 A1	05-10-2000
			JP 2002541338 T	03-12-2002
			PL 350906 A1	10-02-2003
EP 0700673	A	13-03-1996	EP 0700673 A1	13-03-1996
			AT 214906 T	15-04-2002
			AU 3411295 A	27-03-1996
			CA 2199480 A1	14-03-1996
			DE 69430242 D1	02-05-2002
			DE 69430242 T2	24-10-2002
			JP 10505521 T	02-06-1998
			WO 9607380 A1	14-03-1996
			ZA 9507575 A	14-05-1996

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82